Thermodynamic Study on the Sublimation of Five Aminomethoxybenzoic Acids

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The Knudsen mass-loss effusion technique was used to measure the vapor pressures at different temperatures of the following aminomethoxybenzoic acids: 2-amino-3-methoxybenzoic acid, between (349.12 and 369.18) K; 2-amino-5-methoxybenzoic acid, between (353.13 and 375.17) K; 3-amino-4-methoxybenzoic acid, between (379.67 and 399.18) K; 3-amino-5-methoxybenzoic acid, between (380.16 and 400.18) K; and 4-amino-3-methoxybenzoic acid, between (373.14 and 395.17) K. From the temperature dependences of the vapor pressure of the crystalline compounds, the standard ($p^o = 10^5$ Pa) molar enthalpies and Gibbs energies of sublimation, at $T = 298.15$ K, were derived. The results allowed the estimation of these two thermodynamic properties for two isomers not studied in this work—2-amino-6-methoxybenzoic acid and 3-amino-2-methoxybenzoic acid. Differential scanning calorimetry was used to measure the temperature and molar enthalpy of fusion of the studied isomers.

Introduction

During the past decade our research group has been investigating the volatility of different aromatic carboxylic acids[1−9] with the aim of understanding the factors that contribute to the observed volatilities. An important part of this study is concerned with substituted benzoic acids.[4−9] In this work, we decided to perform a thermodynamic study on the sublimation of aminomethoxybenzoic acid isomers to compare the results with those obtained through a similar study on the aminomethylbenzoic acid isomers.[7]

Experimental Section

Materials. All the compounds studied in this work are commercial products from Aldrich Chemical Co.: 2-amino-3-methoxybenzoic acid (CAS n. 3177-80-8), 98 %; 2-amino-5-methoxybenzoic acid (CAS n. 6705-03-9), 97 %; 3-amino-4-methoxybenzoic acid (CAS n. 2840-26-8), 98 %; 3-amino-5-methoxybenzoic acid (CAS n. 74165-74-5), 97 %; and 4-amino-3-methoxybenzoic acid (CAS n. 2486-69-3), 98 %. Samples of the compounds were purified by repeated sublimation under reduced pressure ($p = 1$ Pa) previous to the experimental study. The final purity of all isomers was determined as being better than 99 %, by gas chromatography (GC) performed on an Agilent 4890D gas chromatograph equipped with an HP-5 column, cross-linked, 5 % diphenyl and 95 % dimethylpolysiloxane (15 m, 0.530 mm i.d., 1.5 μm film thickness), with nitrogen as the carrier gas and an FID detector.

Differential Scanning Calorimetry. DSC was used to detect possible phase transitions in the crystalline phase and to determine the temperatures and enthalpies of fusion of the purified samples. The measurements were made in hermetically sealed steel crucibles using a power compensated differential scanning calorimeter, Setaram DSC 141, under a heating rate of $3.3 \cdot 10^{-2}$ K·s^{-1}. The calibration of the power scale of the calorimeter was performed using high-purity indium (mass fraction > 0.99999). The temperature scale of the calorimeter was calibrated by measuring the melting temperature of the following high purity reference materials: naphthalene, benzoic acid, and indium.[10] For each compound, at least four independent runs were performed. Mean results and experimental uncertainties (calculated as twice the standard deviations) of the temperatures (observed at the onset of the calorimetric peaks) of fusion, T_{fus}, and of the molar enthalpies of fusion, $\Delta^l_{cr}H^o_m(T_{fus})$ are presented in Table 1. No crystalline transitions were detected between the temperature 298 K and the temperature of fusion of the studied compounds.

Table 1. Temperatures of Fusion, T_{fus} (Onset), and Molar Enthalpies of Fusion, $\Delta^l_{cr}H^o_m(T_{fus})$, of the Studied Compounds[a]

compound	T_{fus} / K	$\Delta^l_{cr}H^o_m(T_{fus})$ / kJ·mol^{-1}
2-amino-3-methoxybenzoic acid	443.01 ± 0.26	24.21 ± 0.05
2-amino-5-methoxybenzoic acid	424.96 ± 0.38	22.88 ± 0.04
3-amino-4-methoxybenzoic acid	477.87 ± 0.24	25.34 ± 0.06
3-amino-5-methoxybenzoic acid	456.94 ± 0.40	22.40 ± 0.08
4-amino-3-methoxybenzoic acid	462.35 ± 0.76	25.27 ± 0.16

[a] Experimental uncertainties were calculated as twice the standard deviations.

Table 2. Areas and Clausing Factors of the Effusion Orifices[a]

	orifice	A_o/mm^2	w_o
small orifices	A_1	0.502	0.988
	A_2	0.509	0.988
	A_3	0.497	0.989
medium orifices	B_4	0.774	0.991
	B_5	0.783	0.991
	B_6	0.792	0.991
large orifices	C_7	1.099	0.992
	C_8	1.125	0.992
	C_9	1.131	0.992

[a] $w_o = \{1 + (3l/8r)\}^{-1}$, where l is the length of the effusion orifice ($l = 0.0125$ mm) and r is its radius.

Vapor Pressure Measurements. A mass-loss Knudsen-effusion apparatus which enables the simultaneous operation of nine effusion cells, contained in cylindrical holes inside three temperature-controlled aluminum blocks, was used to measure

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Table 3. Effusion Results for the Studied Compounds[a]

			m/mg			*p*/Pa		
T/K	*t*/s	orifices	m_S	m_M	m_L	p_S	p_M	p_L
			2-amino-3-methoxybenzoic acid					
349.12	27023	$A_1-B_4-C_7$	5.00	7.60	10.80	0.123	0.121	0.121
351.18	27023	$A_2-B_5-C_8$	6.23	9.52	13.58	0.152	0.150	0.149
353.19	27023	$A_3-B_6-C_9$	7.73	11.90	16.70	0.194	0.186	0.183
355.13	18421	$A_1-B_4-C_7$	6.42	9.94	13.96	0.234	0.235	0.232
357.18	18421	$A_2-B_5-C_8$	8.24	12.20	17.42	0.297	0.285	0.283
359.12	11775	$A_1-B_4-C_7$	6.32	9.59	13.60	0.362	0.356	0.355
360.13	14563	$A_1-B_4-C_7$	8.77	13.45	18.94	0.407	0.404	0.400
361.16	11775	$A_2-B_5-C_8$	7.87	11.88	16.87	0.446	0.437	0.431
363.18	11775	$A_3-B_6-C_9$	9.47	14.73	20.68	0.552	0.537	0.527
367.18	14563	$A_2-B_5-C_8$	18.32	27.46	38.81	0.847	0.823	0.808
369.18	14563	$A_3-B_6-C_9$	21.72	33.75	47.31	1.031	1.004	0.983
			2-amino-5-methoxybenzoic acid					
353.13	16406	$A_1-B_4-C_7$	2.46		5.42	0.100		0.101
355.15	27160	$A_1-B_4-C_7$	5.30	8.00	11.60	0.131	0.128	0.130
357.20	27160	$A_2-B_5-C_8$		10.05	14.35		0.159	0.158
359.18	27160	$A_3-B_6-C_9$	8.05	12.45	17.73	0.202	0.196	0.195
361.15	16649	$A_1-B_4-C_7$	6.18	9.45	13.64	0.251	0.249	0.252
363.20	16649	$A_2-B_5-C_8$	7.85	11.67	16.86	0.316	0.304	0.306
365.18	16649	$A_3-B_6-C_9$	9.29	14.54	20.80	0.384	0.376	0.376
367.16	16406	$A_2-B_5-C_8$	11.67	17.22	24.18	0.479	0.458	0.447
369.18	16406	$A_3-B_6-C_9$	13.69	21.30	29.96	0.577	0.562	0.553
371.14	10915	$A_1-B_4-C_7$	11.51	17.30	25.02	0.723	0.704	0.716
373.17	10915	$A_2-B_5-C_8$	14.44	21.42	30.53	0.898	0.864	0.856
375.17	10915	$A_3-B_6-C_9$	16.85	26.22	37.18	1.076	1.049	1.039
			3-amino-4-methoxybenzoic acid					
379.67	27357	$A_1-B_4-C_7$	5.51	8.40	11.71	0.140	0.138	0.135
381.72	27357	$A_2-B_5-C_8$	6.92	10.41	14.53	0.174	0.169	0.164
383.68	27357	$A_3-B_6-C_9$	8.33	12.68	17.64	0.215	0.205	0.199
385.16	19421	$A_1-B_4-C_7$	7.01	10.59		0.252	0.247	
387.19	19421	$A_2-B_5-C_8$	8.61	12.93	18.11	0.306	0.298	0.290
389.18	19421	$A_3-B_6-C_9$	10.45	15.86	22.07	0.382	0.363	0.353
391.17	13178	$A_1-B_4-C_7$	8.52			0.455		
393.21	13178	$A_2-B_5-C_8$	10.74	16.25	22.48	0.568	0.557	0.536
395.18	12884	$A_1-B_4-C_7$	12.71	18.99		0.698	0.676	
397.20	12884	$A_2-B_5-C_8$	15.31	23.00	32.08	0.832	0.811	0.786
399.18	12884	$A_3-B_6-C_9$	18.43	27.67	38.53	1.028	0.967	0.941
			3-amino-5-methoxybenzoic acid					
380.16	27117	$A_1-B_4-C_7$	4.90	7.40		0.125	0.123	
381.19	27117	$A_2-B_5-C_8$	5.45	8.21	11.47	0.138	0.135	0.131
383.18	27117	$A_3-B_6-C_9$	6.70	10.05	13.76	0.174	0.164	0.156
385.16	20482	$A_1-B_4-C_7$	6.35	9.43	12.95	0.217	0.208	0.201
387.20	20482	$A_2-B_5-C_8$	7.97	11.56	15.94	0.269	0.253	0.242
389.16	16308	$A_1-B_4-C_7$	7.54	11.31	15.37	0.325	0.316	0.301
393.19	11805	$A_2-B_5-C_8$	8.66	12.79	17.78	0.511	0.490	0.473
395.18	11805	$A_3-B_6-C_9$	10.41	15.58	21.50	0.631	0.591	0.570
397.18	11770	$A_1-B_4-C_7$	12.83			0.773		
399.19	11770	$A_2-B_5-C_8$	15.37	22.93	32.09	0.917	0.887	0.862
400.18	16308	$A_3-B_6-C_9$	22.72	34.02	47.94	1.003	0.940	0.926
			4-amino-3-methoxybenzoic acid					
373.14	18909	$A_1-B_4-C_7$	2.83	4.32	6.16	0.103	0.102	0.102
375.15	22147	$A_1-B_4-C_7$	4.16	6.29	8.91	0.130	0.127	0.126
377.18	22147	$A_2-B_5-C_8$	5.30	7.80	11.00	0.163	0.156	0.153
379.17	22147	$A_3-B_6-C_9$	6.21	9.68	13.43	0.196	0.192	0.186
381.17	18909	$A_2-B_5-C_8$	6.90	10.18	14.20	0.250	0.240	0.232
383.18	18909	$A_3-B_6-C_9$	8.07			0.301		
385.16	14408	$A_1-B_4-C_7$	7.92	11.97	16.95	0.384	0.376	0.374
387.17	14408	$A_2-B_5-C_8$	9.92	14.61	16.55	0.476	0.455	0.444
389.16	11048	$A_1-B_4-C_7$	9.24	13.90	19.70	0.587	0.573	0.570
391.17	11048	$A_2-B_5-C_8$	11.51	17.06	23.92	0.724	0.696	0.678
393.17	11048	$A_3-B_6-C_9$	13.37	20.80	29.20	0.864	0.841	0.826
395.17	14408	$A_3-B_6-C_9$	20.88	32.32	44.67	1.037	1.005	0.971

[a] Results related to the small (A_1, A_2, A_3), medium (B_4, B_5, B_6), and large (C_7, C_8, C_9) effusion orifices are denoted, respectively, by the subscripts S, M, and L.

the vapor pressure of the purified crystalline samples of each of the five aminomethoxybenzoic acids at three different temperatures. During an effusion experiment, each aluminum block is kept at a constant temperature, different from the other two blocks, and contains three effusion cells with effusion orifices of different areas: one "*small*" ($A_o \approx 0.5$ mm^2: series A), one "*medium*" ($A_o \approx 0.8$ mm^2: series B), and one "*large*" ($A_o \approx 1.1$ mm^2: series C). The temperature of each block is measured using a platinum resistance thermometer Pt100 class 1/10 (in a four wire connection) previously calibrated by

Table 4. Experimental Results for the Studied Compounds where *a* and *b* Are from the Clausius−Clapeyron Equation $\ln(p/\text{Pa}) = a - b(\text{K}/T)$ and $b = \Delta_{cr}^{g}H_m^o(<T>)/R$[a,b]

effusion orifices	*a*	*b*	<*T*> / K	$\Delta_{cr}^{g}H_m^o$ (<*T*>) / kJ·mol^{-1}	$\Delta_{cr}^{g}H_m^o$ (298.15 K) / kJ·mol^{-1}	$\Delta_{cr}^{g}G_m^o$ (298.15 K) / kJ·mol^{-1}	R^2
			2-amino-3-methoxybenzoic acid				
S	37.15 ± 0.16	13705 ± 58		113.9 ± 0.5	116.1 ± 0.5	50.59 ± 0.08	0.9998
M	36.91 ± 0.20	13626 ± 72		113.3 ± 0.6	115.5 ± 0.6	50.53 ± 0.10	0.9997
L	36.67 ± 0.24	13545 ± 87		112.6 ± 0.7	114.8 ± 0.7	50.45 ± 0.12	0.9996
mean	36.91 ± 0.24	13625 ± 82	359.15	113.3 ± 0.7	115.5 ± 0.8	50.52 ± 0.12	
			2-amino-5-methoxybenzoic acid				
S	37.91 ± 0.20	14193 ± 73		118.0 ± 0.6	120.4 ± 0.6	52.79 ± 0.11	0.9997
M	37.45 ± 0.15	14033 ± 55		116.7 ± 0.5	119.1 ± 0.5	52.61 ± 0.08	0.9998
L	37.27 ± 0.33	13968 ± 119		116.1 ± 1.0	118.5 ± 1.0	52.51 ± 0.18	0.9993
mean	37.54 ± 0.28	14065 ± 100	364.15	116.9 ± 0.8	119.3 ± 0.8	52.64 ± 0.16	
			3-amino-4-methoxybenzoic acid				
S	38.70 ± 0.18	15440 ± 71		128.4 ± 0.6	131.7 ± 0.6	61.39 ± 0.14	0.9998
M	38.32 ± 0.26	15302 ± 102		127.2 ± 0.9	130.5 ± 0.8	61.20 ± 0.20	0.9996
L	38.11 ± 0.22	15236 ± 84		126.7 ± 0.7	130.0 ± 0.7	61.16 ± 0.17	0.9998
mean	38.38 ± 0.26	15326 ± 100	389.42	127.4 ± 0.8	130.7 ± 0.8	61.25 ± 0.20	
			3-amino-5-methoxybenzoic acid				
S	40.03 ± 0.27	16009 ± 104		133.1 ± 0.9	136.4 ± 0.9	62.84 ± 0.20	0.9996
M	39.71 ± 0.24	15900 ± 95		132.2 ± 0.8	135.5 ± 0.8	62.73 ± 0.19	0.9997
L	39.92 ± 0.30	16000 ± 116		133.0 ± 1.0	136.4 ± 1.0	63.03 ± 0.23	0.9995
mean	39.89 ± 0.32	15970 ± 122	390.17	132.8 ± 1.0	136.1 ± 1.0	62.87 ± 0.24	
			4-amino-3-methoxybenzoic acid				
S	39.55 ± 0.28	15605 ± 106		129.8 ± 0.9	132.8 ± 0.9	60.62 ± 0.20	0.9995
M	39.35 ± 0.25	15539 ± 97		129.2 ± 0.8	132.3 ± 0.8	60.56 ± 0.18	0.9996
L	38.86 ± 0.36	15360 ± 138		127.7 ± 1.2	130.8 ± 1.2	60.30 ± 0.26	0.9994
mean	39.25 ± 0.34	15501 ± 132	384.15	128.9 ± 1.2	132.0 ± 1.2	60.49 ± 0.24	

[a] $\Delta_{cr}^{g}H_m^o$(298.15 K) and $\Delta_{cr}^{g}G_m^o$(298.15 K) were derived from Clarke Glew eq 2 considering the reference pressure $p^o = 0.1$ MPa. [b] Experimental uncertainties of the selected values (mean values) were calculated as twice the standard deviation.

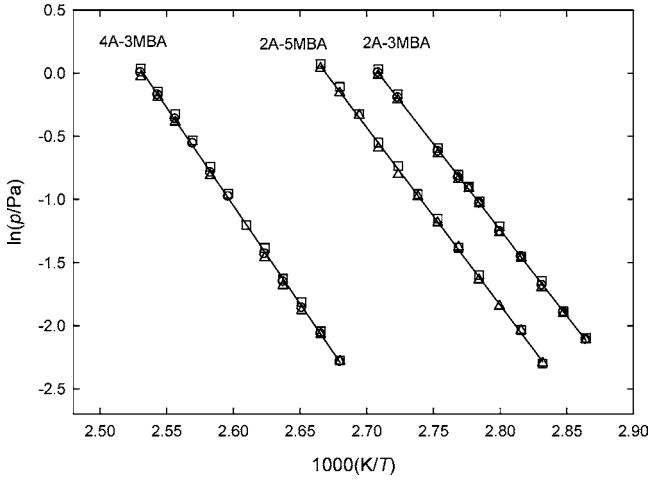


Figure 1. Plots of ln *p* against 1/*T* for 2-amino-3-methoxybenzoic acid (2A-3MBA), 2-amino-5-methoxybenzoic acid (2A-5MBA), and 4-amino-3-methoxybenzoic acid (4A-3MBA). □, small effusion orifices; ○, medium effusion orifices; Δ, large effusion orifices.

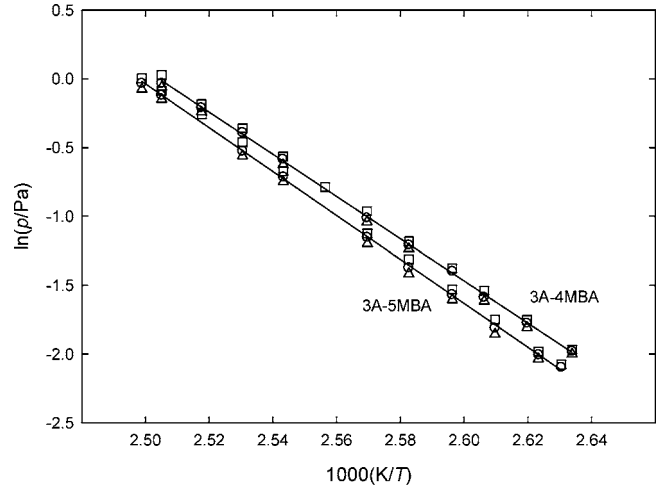


Figure 2. Plots of ln *p* against 1/*T* for 3-amino-4-methoxybenzoic acid (3A-4MBA) and 3-amino-5-methoxybenzoic acid (3A-5MBA). □, small effusion orifices; ○, medium effusion orifices; Δ, large effusion orifices.

comparison with an SPRT (25 Ω; Tinsley, 5187 A). The detailed description of this apparatus and the results obtained by measuring vapor pressures between (0.1 and 1) Pa of benzoic acid, phenanthrene, anthracene, benzanthrone, and 1,3,5-triphenylbenzene were published before.[11] Both the measured vapor pressures and the derived enthalpies of sublimation were in excellent agreement with literature results and recommended values for those compounds.

For the effusion experiments, the loss of mass of the samples during a convenient effusion time period *t* is determined by weighing the effusion cells to ± 0.01 mg before and after the effusion period. For the temperature *T*, measured with an accuracy of ± 0.01 K, the vapor pressure *p* of the crystalline sample contained in each effusion cell is calculated by eq 1, where *m* is the sublimed mass during the effusion time period *t*, *M* is the molar mass of the effusing vapor, *R* is the gas constant, A_o is the area of the effusion orifice, and w_o is the respective Clausing factor. The exact areas and Clausing factors of each used effusion orifice in platinum foil of 0.0125 mm thickness are given in Table 2. The accuracy of the measured pressures is estimated to be better than ± 0.01 Pa.

$$p = (m/A_o w_o t) \cdot (2\pi RT/M)^{1/2} \quad (1)$$

Results and Discussion

Table 3 presents, for all the aminomethoxybenzoic acids, the experimental results obtained from each effusion cell at each studied temperature. Table 4 presents for the three series of

Table 5. Standard Thermodynamic Properties of Sublimation at $T = 298.15$ K of Methylbenzoic Acids, Methoxybenzoic Acids, Aminomethylbenzoic Acids, and Aminomethoxybenzoic Acids

	$\Delta_{cr}^{g}H_{m}^{0}$	$\Delta_{cr}^{g}S_{m}^{0}$	$\Delta_{cr}^{g}G_{m}^{0}$	$\Delta_{cr}^{g}C_{p,m}^{0}$	
	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	ref
2-methylbenzoic acid	95.8 ± 0.2	201.5 ± 0.7	35.73 ± 0.02	−20	*a*
3-methylbenzoic acid	96.8 ± 0.4	200 ± 1	37.10 ± 0.02	−20	*a*
4-methylbenzoic acid	97.8 ± 0.6	192 ± 2	40.42 ± 0.02	−20	*a*
2-methoxybenzoic acid	105.6 ± 0.8	213 ± 3	42.12 ± 0.06	−30	*b*
3-methoxybenzoic acid	108.3 ± 0.8	222 ± 3	42.25 ± 0.06	−30	*b*
4-methoxybenzoic acid	111.2 ± 1.2	212 ± 4	47.96 ± 0.16	−30	*b*
2-amino-3-methylbenzoic acid	107.3 ± 1.2	204 ± 4	46.27 ± 0.18	−29	*c*
2-amino-3-methoxybenzoic acid	115.5 ± 0.8 (118.8)	218 ± 3	50.52 ± 0.12 (51.42)	−35	*d*
2-amino-5-methylbenzoic acid	110.6 ± 1.2	210 ± 4	47.66 ± 0.18	−29	*c*
2-amino-5-methoxybenzoic acid	119.3 ± 0.8 (122.1)	224 ± 3	52.64 ± 0.16 (52.81)	−35	*d*
2-amino-6-methylbenzoic acid	116.1 ± 2.4	231 ± 8	47.26 ± 0.34	−29	*c*
2-amino-6-methoxybenzoic acid	[123.3]		[53.18]		*e*
3-amino-2-methylbenzoic acid	127.8 ± 1.6	240 ± 5	56.30 ± 0.32	−29	*c*
3-amino-2-methoxybenzoic acid	[136.2]		[62.73]		*e*
3-amino-4-methylbenzoic acid	119.4 ± 1.8	220 ± 6	53.74 ± 0.34	−29	*c*
3-amino-4-methoxybenzoic acid	130.7 ± 0.8 (132.8)	233 ± 3	61.25 ± 0.20 (61.28)	−35	*d*
3-amino-5-methoxybenzoic acid	136.1 ± 1.0	246 ± 3	62.87 ± 0.24	−35	*d*
4-amino-3-methylbenzoic acid	122.0 ± 1.4	223 ± 5	55.50 ± 0.28	−29	*c*
4-amino-3-methoxybenzoic acid	132.0 ± 1.2 (133.5)	240 ± 4	60.49 ± 0.24 (60.65)	−35	*d*

[a] Values recalculated in this work from the experimental vapor pressure results presented in ref 17. The value $\Delta_{cr}^{g}C_{p,m}^{0} = -20$ J·K^{-1}·mol^{-1} was calculated from the value $C_{p,m}^{0}(g) = 149$ J·K^{-1}·mol^{-1}[18] and from $C_{p,m}^{0}(cr) = 169$ J·K^{-1}·mol^{-1}.[19] [b] Values calculated in this work from the experimental vapor pressure results presented in ref 16. The value $\Delta_{cr}^{g}C_{p,m}^{0} = -30$ J·K^{-1}·mol^{-1} was estimated from $C_{p,m}^{0}(g) = 167$ J·K^{-1}·mol^{-1},[18] using eq 3. [c] Experimental uncertainties recalculated in this work from the results presented in ref 7. [d] This work (values inside parentheses are estimated values). [e] Values calculated in this work using the estimation scheme, eq 5, and eq 6.

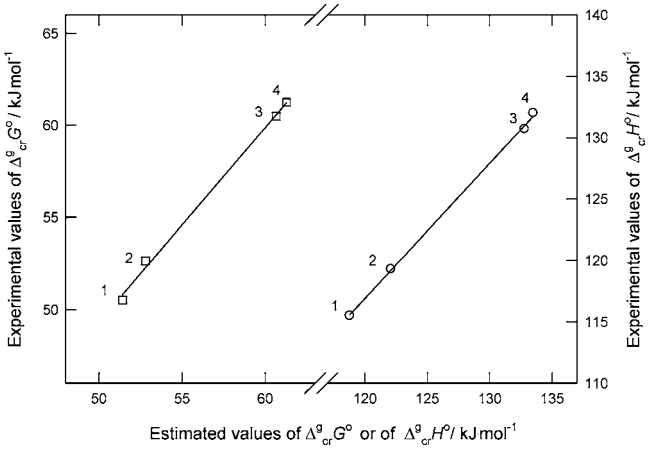


Figure 3. Correlations between estimated and experimental values of enthalpy (circle) and standard Gibbs energy (square) of sublimation for 2-amino-3-methoxybenzoic acid (1), 2-amino-5-methoxybenzoic acid (2), 4-amino-3-methoxybenzoic acid (3), and 3-amino-4-methoxybenzoic acid (4).

effusion orifices the detailed parameters of the Clausius−Clapeyron equation, $\ln(p/\text{Pa}) = a - b(\text{K}/T)$, where a is a constant and $b = \Delta_{cr}^{g}H_{m}^{o}(\langle T\rangle)/R$, and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T = \langle T\rangle$. The values of the standard enthalpy and Gibbs energy of sublimation at the reference temperature $\theta = 298.15$ K are also presented in this table. These values were derived fitting the experimental results of the vapor pressures by the Clarke and Glew eq 2.[12]

$$R\cdot\ln\left(\frac{p}{p^{o}}\right) = -\frac{\Delta_{cr}^{g}G_{m}^{o}(\theta)}{\theta} + \Delta_{cr}^{g}H_{m}^{o}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{cr}^{g}C_{p,m}^{o}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (2)$$

where p is the vapor pressure at the temperature T; p^{o} is a selected reference pressure ($p^{o} = 10^{5}$ Pa in this work); θ is a selected reference temperature ($\theta = 298.15$ K in this work); R is the molar gas constant; and $\Delta_{cr}^{g}C_{p,m}^{o}(\theta)$ is the difference in molar heat capacity at constant pressure between the gaseous and the crystalline phase.

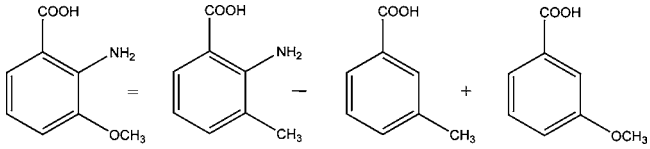
The values of $\Delta_{cr}^{g}C_{p,m}^{o}(\theta)$ inserted in eq 2 were estimated from the gas phase molar heat capacity of the isomer 3-amino-5-methoxybenzoic acid, calculated at $\theta = 298.15$ K as $C_{p,m}^{o}(g) = 192.49$ J·K^{-1}·mol^{-1} using computational chemistry. The geometry optimization, as well as the fundamental vibrational frequency calculation, were performed using density functional theory (DFT) with the hybrid exchange correlation functional B3LYP at the 6-311++G(d,p) level of theory. The frequencies were scaled using the scale factor of 0.9688,[13] and the Gaussian 03 software package[14] was used for the necessary calculations. The value $\Delta_{cr}^{g}C_{p,m}^{o}(\theta) = -35$ J·K^{-1}·mol^{-1} was estimated for this isomer using eq 3, and the same value was assumed for the other isomers. This equation is a rearrangement of eq 4 proposed by Chickos et al.[15] for estimation of $\{C_{p,m}^{o}(g) - C_{p,m}^{o}(cr)\}$, at the temperature 298.15 K, from$C_{p,m}^{o}(cr)$ values (from eq 4, $C_{p,m}^{o}(cr) = \{C_{p,m}^{o}(g) + 0.75\}/0.85$; replacing this expression in eq 4 yields eq 3)

$$\Delta_{cr}^{g}C_{p,m}^{o}(\theta) = -\{0.9 + 0.176C_{p,m}^{o}(g)\}\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad (3)$$

$$\Delta_{cr}^{g}C_{p,m}^{o}(\theta) = -\{0.75 + 0.15C_{p,m}^{o}(cr)\}\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad (4)$$

The plots of $\ln(p/\text{Pa})$ versus $1/T$ for the five studied compounds are presented in Figures 1 and 2.

As may be observed from the values presented in Table 5, the effect on both the enthalpy of sublimation and the Gibbs energy of the substitution of a methyl group by a methoxy group in an isomer of aminomethylbenzoic acid is similar to the same substitution performed in methylbenzoic acids, respecting the relative positions of the substituents. So, we compared the experimental results of enthalpy and standard Gibbs energy of sublimation of the studied isomers with the values estimated from published results for aminomethylbenzoic acid isomers,[7] methoxybenzoic acids,[16] and methylbenzoic acids,[17] using the scheme that is exemplified for one of the isomers



The values presented in Table 5 for the aminomethoxybenzoic acid isomers show an excellent agreement between experimental results and estimated ones (inside parentheses) for the standard Gibbs energy of sublimation and a good agreement for the values of enthalpy of sublimation—the estimated values of enthalpy of sublimation are only (1.5 to 3.3) kJ·mol^{-1} higher than the experimental ones. Figure 3 presents plots of estimated versus experimental values of these two thermodynamic properties for the aminomethoxybenzoic acids. From these plots, the correlations 5 and 6, where $\Delta_{cr}^{g}H_{m}^{o}(\theta)$ and $\Delta_{cr}^{g}G_{m}^{o}(\theta)$ are expressed in kJ·mol^{-1}, were derived

$$\Delta_{cr}^{g}H_{m}^{o}(\theta)_{exp} = -15.3 + 1.101\Delta_{cr}^{g}H_{m}^{o}(\theta)_{est} \quad (5)$$

$$\Delta_{cr}^{g}G_{m}^{o}(\theta)_{exp} = -3.47 + 1.056\Delta_{cr}^{g}G_{m}^{o}(\theta)_{est} \quad (6)$$

Using these correlations and the above referred estimation schemes, the following results were calculated for two isomers of aminomethoxybenzoic acid not studied in the present work:

2-amino-6-methoxybenzoic acid, $\Delta_{cr}^{g}H_{m}^{o}(298.15\ K) = 123.3$ kJ·mol^{-1}; $\Delta_{cr}^{g}G_{m}^{o}(298.15\ K) = 53.18$ kJ·mol^{-1};

3-amino-2-methoxybenzoic acid, $\Delta_{cr}^{g}H_{m}^{o}(298.15\ K) = 136.2$ kJ·mol^{-1}; $\Delta_{cr}^{g}G_{m}^{o}(298.15\ K) = 62.73$ kJ·mol^{-1}.

The volatility of a crystalline compound, at a certain temperature T, decreases with increasing values of $\Delta_{cr}^{g}G_{m}^{o}(T)$, or considering that $\Delta_{cr}^{g}G_{m}^{o}(T) = \Delta_{cr}^{g}H_{m}^{o}(T) - T\Delta_{cr}^{g}S_{m}^{o}(T)$, the volatility decreases with increasing $\Delta_{cr}^{g}H_{m}^{o}(T)$ and with decreasing $\Delta_{cr}^{g}S_{m}^{o}(T)$. The volatility of the previously studied aminomethylbenzoic acid isomers is higher than the volatility of the related isomers of aminomethoxybenzoic acid studied in this work. This difference in volatility is clearly due to enthalpic factors—the lower volatility of the methoxy-substituted aminobenzoic acids, compared with methyl-substituted aminobenzoic acids in identical positions, is due to the higher enthalpies of sublimation of the former, despite their higher entropies of sublimation.

The 2-aminobenzoic acids with methyl or methoxy substituent groups present enthalpies of sublimation about (15 to 16) kJ·mol^{-1} lower than the corresponding 3-amino and 4-amino methyl- or methoxy-substituted benzoic acids. This fact seems to indicate the existence of an intramolecular hydrogen bonding in the 2-amino isomers that may result in a stabilizing effect in the gas phase and also contribute to the weakening of the intermolecular interactions between the carboxylic groups in the crystalline phase. Both effects yield lower enthalpies of sublimation, but the question of the relevancy of each one is not conclusive analyzing just the results derived in the present study.

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